ARTHUR LOKE & PARTNERS
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Your Ref: PCT/SG2003/000136

Our Ref: A3/0413 PK/rs

27 August 2004

URGENT

By Fax (61 2 6283 7999) & Post

The Commissioner of Patents
Australian Patent Office
PO Box 200,
Woden Act 2606,
Australia

Attention : Ms Tharu Fernando

Dear Sir

International Application No PCT/SG2003/000136 filed on 3 June 2003
Claiming Priority from Singapore Application No 200203314-0 filed on 4 June 2002
Invention Title : Method for Electroless Metalisation of Polymer Substrate
Applicants : (1) Agency for Science, Technology and Research
(by assignment from Institute of Materials Research and Engineering)
(2) BHANGALE Sunil Madhukar
(3) Peter Malcolm MORAN

1. We act for all the Applicants in the captioned international application.

Response to Written Opinion

2. The Applicants have instructed us to respond to the Written Opinion with mailing date 14 October 2003 by submitting:

   a. amendments to the specification; and

   b. comments on the novelty and inventive step of the claims which have been objected to.

Amendments

3. The Applicants wish to make amendments to pages 2 and 3 of the Description and page 9 of the Claims under Article 34(2). Accordingly, we **lodge*** herewith substitute pages 2, 3 and 9, together with marked-up copies thereof.

9 Temasek Boulevard #23-01 Suntec Tower Two Singapore 038989
Tel : +65 6737 1234 Fax : +65 6339 4991
Email : alplaw@arthurloke.com.sg Website : www.arthurloke.com.sg

4. As will be noted:

   a. independent claim 1 has been amended to more clearly specify the sequential order of the steps of the relevant method; and

   b. the relevant consistory clause (on pages 2 and 3) has been amended to correspond with the above.

Examiner's Opinion

5. In the Written Opinion, the Examiner states that the method defined in claim 1 and the subsidiary claims lacks novelty and inventive step in light of 3 cited prior art documents. These are discussed below.

Citation US 4,517,254

6. Citation US 4,517,254 is in respect of an invention entitled "adhesive metallisation of polyimide". This document describes a process for the adhesive metallisation of polyimide through pre-treating of the polyimide and subsequent activation followed by the optional step of chemical metallisation. US 4,517,254 is clearly directed to the initial pre-treatment step in which the polyimide substrate is treated (or pre-treated) with an "aqueous solution of alkylhydroxide and an organic nitrogen compound". The organic nitrogen compound is an essential feature of the aqueous solution and the specification goes into great detail in itemising suitable organic nitrogen compounds. The organic nitrogen compounds appear to be included in the solution for the purpose of ensuring that the desired degree of adhesion is attained between the polyimide and any subsequently deposited metal layer.

7. In the subject application, the polymer film is pre-treated with a basic solution (typically in NaOH or KOH). The solution does not contain any organic nitrogen compounds for the purpose of improving adhesion. In the subject invention, the desired degree of adhesion is achieved without any organic nitrogen compounds, simply by following the steps of the claimed method.

8. Another feature of the subject invention is that, following the pre-treatment step, the polymer film has applied to it an aqueous seeding solution comprising polymer-stabilised catalyst particles. Although US 4,517,254 does mention activation by a catalyst (namely a palladium containing activator), it makes no mention whatsoever of the catalyst particles being polymer-stabilised. This feature of having the catalyst particles polymer-stabilised is a feature which is not anticipated by US 4,517,254.

9. In light of the above, it is submitted that the claimed invention is novel and inventive over US 4,517,254.

Citation US 4,770,899

10. Citation US 4,770,899 is for an invention entitled "method of coating copper conductors on polyimide with a corrosion resistant metal and module produced thereby". The relevant method described in this patent describes dipping a polyimide substrate, having a plurality of spaced apart copper conductors, into a solution of palladium chloride. After this step, the substrate is then dipped into a solution of sodium hydroxide, followed by dipping into an electroless plating solution for the coating of a layer of cobalt thereon. This method is very different from the method of the subject application. For instance, in the subject application, the method involves – prior to the step of applying the catalyst particles - the step of pre-treating the polymer substrate with a basic solution. This step is not disclosed in US 4,770,899. Although US 4,770,899 does disclose a subsequent step of treating the substrate with a solution of sodium hydroxide, this is done following the step of dipping the substrate into the solution of palladium chloride (being the catalyst). In US 4,770, 899, the purpose of dipping the substrate into the sodium hydroxide solution is to deactivate the substrate. In the subject application, the purpose of pre-treating the substrate with the basic solution is so as to promote seeding of the catalyst particles (not to deactivate the substrate).

11. In order to further differentiate the claimed invention from the disclosure of US 4,770,899, claim 1 of the subject application has been amended to more clearly specify the correct sequential order of the process steps.

12. It is further noted that the subject matter of the disclosure in US 4,770,899 is directed towards a very different application, namely the coating of copper conductors, which are already plated on a polyimide substrate, with another metal such as cobalt (in order to protect the copper from corrosion). This citation does not deal with the metallising of polyimide as such.

13. In light of the above, it is submitted that the claimed invention is novel and inventive over US 4,770,899.

Citation JP 07216553

14. In the Written Opinion, it is further stated that the invention is anticipated by JP 07216553. With respect, this citation in no way discloses the method of the subject invention. For example, the citation makes no mention whatsoever of the relevant catalyst particles being "polymer-stabilised" which is a feature of the subject method.

The method of the citation also involves an additional step of etching the polyimide surface prior to the alkali solution treatment. This step is not included (or appropriate) in the method of the subject application.

15. The citation also specifies an additional step of activating the applied catalyst. No such further activation step is required in the method of the subject application.

16. Also, claim 5 of the subject application specifies that the catalyst comprises palladium particles. The above citation makes no reference to the catalyst being palladium particles.

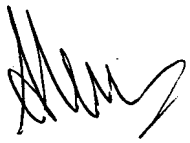
17. In light of the above, it is submitted that the claimed invention is novel and inventive over US 4,770,899.

Concluding Remarks

18. We trust that a clear International Preliminary Examination Report (IPER) will be issued on this application. If the amendments to the specification and the above submissions have not addressed the prior art concerns, the Applicants would appreciate an opportunity to respond to a further Written Opinion.

19. The IPER has to be established by 4 October 2004. The Applicants hope that the Examiner will consider this Response and send to us the examination results (by both fax and post) on an **expedited basis**. Thank you for your assistance.

Yours faithfully



PATSY KOH
DID : +65 6434 2223
Fax : +65 6339 4991
Email : patsykoh@arthurloke.com.sg

Enclosures

adhesive used causes difficulties in laser drilling of micro-vias. Also it wastes metal.

Another means of attempting to improve adhesion has been by coating a liquid polyimide (or its precursor polyamic acid) onto a roughened metal foil (eg copper foil), followed by curing. However, fine line circuitry is once again difficult to achieve owing to the thickness of the metal foil.

Another known method for attempting to improve adhesion is the sputtering of a thin layer of chromium onto a polymer surface. A thin layer of copper is then sputtered onto the chromium layer. This copper layer is then thickened using electroplating. Although this method is able to produce fine line circuitry (by the use of a photoresist before the electroplating step) the sputtering steps are expensive and time consuming.

Also, in all of the above methods, the drilling of micro-vias through the metal coated polymer film is difficult. Also, after drilling, the micro-vias need to be plated separately.

Another technique to make metal-clad polymer films is electroless plating. However, the polymer surface needs to be activated (seeded) with a catalyst to initiate electroless plating. For instance, it has been found that palladium (Pd) is the most effective catalyst to initiate electroless plating.

The present invention is directed towards an improved method for activating a polymer substrate for electroless plating so as to achieve good adhesion between the substrate and a subsequently applied metal coating.

Summary of the invention

According to a first embodiment of this invention, there is provided a method of activating and metallising an aromatic polymer film including the steps of:

- pre-treating a first surface of the film with a basic solution;
- following the pre-treatment step, applying to said first surface an aqueous seeding solution comprising polymer-stabilised catalyst particles; and

- then immersing the film in an electroless plating bath comprising ions of a desired metal so as to deposit a layer of said metal onto the first surface of said film.

Preferably the basic solution is a solution of sodium hydroxide (NaOH) or, more preferably, potassium hydroxide (KOH). A relatively wide range of concentrations is suitable for this solution (eg. 0.2 to 2M). The basic solution may be applied by immersing the film in a bath of the basic solution. Alternatively, the basic solution may be applied by spraying a layer of the solution onto the first surface of the film. The surface (or surfaces) of the film which is (or are) to be activated should be maintained in contact with the basic solution for a certain period of time, depending upon the molarity and temperature of the basic solution (for example from 1 to 15 minutes for a 1M KOH solution at room temperature). After immersion (or spraying), the basic solution is washed off, preferably with de-ionised water. Application of the basic solution is typically conducted at temperatures of between 20° to 60° Celsius.

In some cases, after treating the polymer film with the basic solution (eg. KOH), the polymer film is subsequently treated with an acidic solution for protonation of the carboxylate ions formed on the surface. It is done by immersing the KOH treated film in an aqueous acid solution for a certain period of time (e.g. 2 to 20 minutes). Later on it is washed with de-ionised water and is dried, usually with flowing air.

It is preferred that the aqueous seeding solution contains polymer-stabilised palladium particles. This stabilisation may be effected by a water-soluble polymer, such as polyvinyl pyrrolidone (PVP) or polyvinyl alcohol (PVA), although PVP is particularly preferred.

Typically the abovementioned palladium particles will have diameters of from 1 to 50 nm, or more preferably, from 2 to 10 nm.

The aqueous seeding solution is typically applied to the film by immersing the film in a bath of the seeding solution. This immersing typically occurs for between 2 and 60 seconds. After this, the film is removed from the bath and

Claims

The claims defining this invention are as follows:

1. A method of activating and metallising an aromatic polymer film including the steps of:
   - pre-treating a first surface of the film with a basic solution ;
   - following the pre-treatment step, applying to said first surface of the film an aqueous seeding solution comprising polymer-stabilised catalyst particles; and
   - then immersing the film in an electroless plating bath comprising ions of a desired metal so as to deposit a layer of said metal onto the first surface of said film.
2. The method of claim 1, wherein the basic solution is a solution of potassium hydroxide.
3. The method of claim 1 or claim 2, wherein after the basic solution treatment step, an acidic solution is applied to said first surface.
4. The method of claim 3 wherein the acidic solution is a solution of protic acid such as hydrochloric acid (HCl) or acetic acid.
5. The method of any one of claims 1 to 4, wherein the aqueous seeding solution comprises polymer-stabilised palladium particles.
6. The method of any one of claims 1 to 5, wherein the catalyst particles are stabilised by a water-soluble polymer.
7. The method of claim 6, wherein the water-soluble polymer is polyvinyl pyrrolidone (PVP) or polyvinyl alcohol (PVA).
8. The method of claim 7, wherein the water-soluble polymer is PVP.
9. The method of any one of claims 5 to 8, wherein the palladium particles have diameters of from 1 to 50 nanometers.
10. The method of any one claims 1 to 9, wherein the desired metal is selected from the group consisting of nickel, copper and gold.

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10. The method of any one claims 1 to 9, wherein the desired metal is selected from the group consisting of nickel, copper and gold.